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# Nitrothiacalixarenes with alkyl groups at the lower rim: design, synthesis and aggregation behaviour at the air–water interface and in solution

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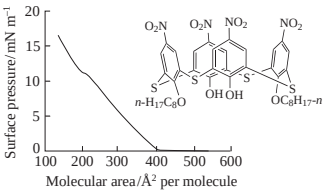
**Di-*n*-octylated tetranitrothiacalix[4]arene, a new multidipolar D-π-A chromophore has been synthesized and the dependence of its aggregation in solution and at the air–water interface on the concentration of solution and spreading solvent has been evaluated.**




A relevant field of modern materials science is the investigation of nonlinear optical properties of noncentrosymmetric structures, which can be used for the storage of holographic memory, signal amplification, as well as the protection of materials against powerful irradiation. The materials based on organic chromophores, which exhibit these properties, are superior to inorganic materials in higher hyperpolarizability and facile modification. However, their remarkable drawback is relatively low photochemical stability, as well as the ability to form centrosymmetric associates, which reduce the magnitude of the dipole moment.[1] One of the possible routes towards the increase in the stability of chromophores and amplification of nonlinear optical effect is the employment of macrocycles such as calixarenes, whose structures allow one to introduce a diverse number of chromophoric fragments at appropriate orientation.[2,3] As exemplified by calixarenes containing nitro and azo fragments, an increase in the hyperpolarizability coefficient as compared to analogous phenol derivatives was predicted by theoretical calculations and experimentally demonstrated.[4–6]

In spite of evident advantages of calixarene scaffold (relatively rigid framework of the molecule, broad opportunities towards regio-, stereo-, and iteroselective functionalization),[7–11] the retention of stereoisomeric form of the macrocycle and the design of ordered films on their basis with a uniaxial orientation of dipoles of molecules is still topical. It is known that one of the factors affecting the stability of stereoisomeric form of macrocycle is the competition between polar groups for the formation of hydrogen bonds.[12] For this reason, the controlled formation of highly organized ultrathin Langmuir films of thiacalixarenes with the given orientation of chromophoric fragments relative to the solid substrate may provide both an increase in thermal stability of multidipolar systems and elimination of the demand to apply an additional electric field (in contrast with corona poled films of chromophore-containing oligomers and polymers)[13,14] during the study of nonlinear optical activity of macrocyclic chromophores.[15,16]

We have recently shown that thiacalix[4]arenes bearing hydroneutral nitrile and hydrophilic crown-ether fragments[17,18] can form organized Langmuir monolayers. In addition, there are examples of the formation of Langmuir monolayers of tetranitrocalix[4]arenes with various alkyl fragments on the lower rim.[19] The aim of this work was to synthesize new macrocyclic chromophore based on nitrothiacalix[4]arene in cone configuration and to optimize the conditions of ultrathin film formation with preorganized macrocycles *via* Langmuir monolayer method.

To synthesize the target product, the sequence of transformations was accomplished, which involves the functionalization of upper and lower rims of thiacalix[4]arene **1** under the conditions of electrophilic aromatic substitution and the Mitsunobu reaction, respectively (Scheme 1).† Due to hydrolytic instability of

† $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Mass spectra were recorded on Bruker Ultraflex III TOF/TOF (MALDI, *p*-nitroaniline matrix) and Amazon X (ESI, DMF solvent) mass spectrometers. IR spectra were acquired on a Bruker Vector-22 IR Fourier spectrometer in KBr pellet. Thiacalixarenes **1** and **2** were synthesized as reported.[20,21]

*25,27-Dihydroxy-26,28-dioctyloxy-5,11,17,23-tetranitro-2,8,14,20-tetrathiacalix[4]arene* **3**. Triphenylphosphine (0.427 g, 1.630 mmol) and octan-1-ol (1.20 ml, 7.400 mmol) were added in one portion to the solution of compound **2** (0.500 g, 0.740 mmol) in toluene (120 ml), and then diethyl azodicarboxylate (0.250 ml, 1.630 mmol) was added dropwise at room temperature; the mixture was stirred at 40 °C for 40 h. After removal of solvent, the residue was washed with ethanol and the target product was isolated as a yellow powder, yield 0.460 g (69%), mp 199 °C (decomp.).